Synthesis, Characterization, X-Ray Structural Analysis, and Iodination Ability of Benzyl(triphenyl)phosphonium Dichloroiodate

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Benzyl(triphenyl)phosphonium dichloroiodate (BTPPICl$_2$), BnPh$_3$P$^+$(ICl$_2$)$^-$, is easily synthesized in a nearly quantitative yield by the addition of BnPh$_3$P$^+$Cl$^-$ to a CH$_2$Cl$_2$ solution of iodine monochloride (ICl). BnPh$_3$P$^+$Cl$^-$ can be prepared by the reaction of Ph$_3$P and BnCl. The compound was characterized by physicochemical and spectroscopic methods (elemental analysis, FT-IR, and ^{1}H-NMR). The use of phosphonium counterion improves the quality of the BTPPICl$_2$ crystals. BTPPICl$_2$ crystallizes in the monoclinic system, and its crystal and molecular structure has been determined at 100(1) K by X-ray diffraction. The structure was solved by the direct method and had refined R value of 0.0637 for 699 reflections ($I > 2\sigma(\mathrm{I})$), space group $P21/n$ with $a = 12.4700(3)$, $b = 13.2196(3)$, $c = 14.4580(3)$ Å, $\beta = 102.6340(10)°$, $V = 2325.67(9)$ Å^3, and $Z = 4$. The I-atom is coordinated by two Cl-atoms as ligands in a linear geometry. This compound is a versatile reagent for the efficient and selective iodination of organic substrates, in particular of aromatic phenols to the corresponding iodo compounds, under mild conditions. To assess the generality of method, a wide variety of phenols with electron-donating and electron-withdrawing substituents were studied. BTPPICl$_2$ is a mild iodination reagent, which offers a new avenue for an expeditious iodination of phenols. The inexpensive, relatively non-toxic reagent, and mild conditions are the positive features of the procedure and reagent.

Introduction. – In this article, we report the synthesis of the benzyl(triphenyl)-phosphonium dichloroiodate (BTPPICl), Bn(Ph)$_3$P$^+$(ICl$_2$)$^-$, as iodination agent and especially the X-ray diffraction data, concerning the crystal and molecular structure of the compound. There were two primary incentives for the selection of BnPh$_3$P$^+$ as counterion. First, quaternary phosphonium ions are often used as phase transfer catalysts. This could make BTPPICl$_2$ a more efficient and reactive agent. Therefore, this compound has been used for quantitative iodination of several organic substrates. It turned out to be more efficient and to possess some advantages over similar iodination agents in terms of the amount of reagent and solvent required, short reaction times, and high yields [1–13]. Second, quaternary ions such as those with phosphorus are used as crystal-growing agents. Hence, use of this counterion improved the quality of the BTPPICl$_2$ crystals. Indeed, the salt crystallized well and was structurally characterized by single-crystal X-ray diffraction. Furthermore, this compound does not react with MeCN, which is a suitable medium for studying kinetics and mechanism.

Results. – $BTPPICl_2$ is an efficient, mild, and versatile reagent for the iodination of phenols. The best reagent/substrate ratio was found to lie between 1.05 and up to 4.05 depending on the number of iodination positions. For example, the ratio for the iodination of phenol to 2,4,6-triiodophenol was 3.05, and 2,6-dimethylphenol to 4-iodo-2,6-dimethylphenol was 1.05. Using too low reagent/substrate ratios for substrates with several positions for the iodination led to mixtures of mono and higher iodination products. An excess reagent/substrate ratio affected neither the yields nor the reaction time. The reaction of corresponding phenols was performed in CH_2Cl_2/MeOH 3:1 at room temperature (*Table 1*).

It is noteworthy to mention that all reactions should be conducted at room temperature, since increasing the reaction temperature above 20° decreases the yields of the reaction, probably due to oxidation [14–17]. To assess the generality of the method, a wide variety of phenols with electron-donating and electron-withdrawing substituents were examined.

$BTPPICl_2$ was crystallized by slow evaporation over a week from a MeCN solution.

Discussion. – Benzyl(triphenyl)phosphonium dichloroiodate ($BTPPICl_2$) can be easily obtained by the addition of $BnPh_3P^+Cl^-$ to a CH_2Cl_2 solution of ICl.

$$BnPh_3P^+Cl^- \;+\; ICl \xrightarrow{CH_2Cl_2,\ 50\ \text{min, r.t.}} BnPh_3P^+(ICl_2)^-$$

The advantages of the new method are: *i*) there is no side-product, *ii*) the reaction is quite fast, *iii*) mild conditions, and *iv*) the accompanied color change, which provides a visual evidence for ascertaining the progress of the reaction.

In summary, $BTPPICl_2$ is an efficient and mild iodination reagent, which offers a new procedure for an expeditious iodination of phenols. The inexpensive, relatively non-toxic reagent and mild conditions are the positive features of the procedure.

$BTPPICl_2$ crystallized in the non-centrosymmetric monoclinic space group *P*21/*n* (*Fig. 1*). The cation and anion moieties were separated from each other and arranged in an alternative AB layering pattern. The I-atom was coordinated by two Cl-atoms as ligands in linear geometry. The results of the X-ray diffraction showed that the structure of this dichloroiodate salt did not form a dimer, trimer, or more multi-nuclear structures in the solid state (*Fig. 2*).

New iodination reagent $BTPPICl_2$ was easily synthesized in a nearly quantitative yield by the addition of $BnPh_3P^+Cl^-$ to a CH_2Cl_2 solution of ICl. The compound was characterized by physicochemical and spectroscopic methods such as CHN analysis, and FT-IR and ^1H-NMR techniques. The use of phosphonium counterion, improves the quality of the $BTPPICl_2$ crystals. $BTPPICl_2$ crystallizes in the tetragonal system, and its crystal and molecular structure has been determined at 100(1) K by X-ray diffraction. The structure was solved by the direct method.

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Table 1. *Iodination of Phenols with BTPPICl$_2$ as an Iodination Agent*

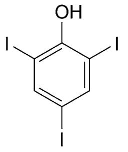
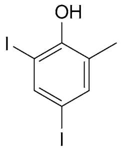
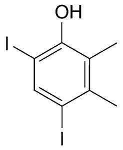
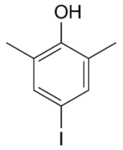
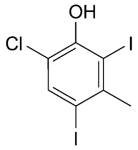
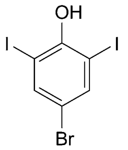
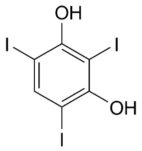
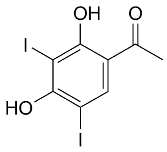
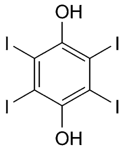
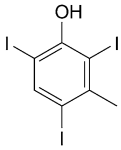
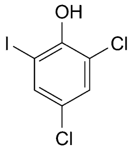
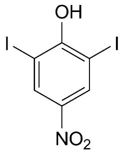
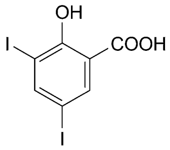
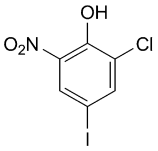
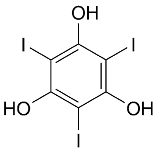
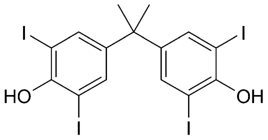
Entry	Product	Reagent/ substrate	Reaction time [min]	M.p. (Lit.) [°]	Yield [%]
1		3.05	150	157–159 ([14]: 158–159)	73
2		2.05	380	65–67 ([15]: 67)	70
3		2.05	330	85	73
4		1.05	220	99–102 ([16]: 102–102.5)	82
5		2.05	200	82–84	86
6		2.05	200	87–89	85
7		3.05	80	148–150 ([17]:149–150)	92
8		2.05	40	120–122	91

Table 1 (cont.)

Entry	Product	Reagent/ substrate	Reaction time [min]	M.p. (Lit.) [°]	Yield [%]
9		4.05	24	106–110	92
10		3.05	200	119–121 ([18]: 121)	89
11		1.05	140	60–62 ([19]: 62)	75
12		2.05	75	156–157 ([20]: 157)	95
13		2.05	30	233–235 ([21]: 233)	91
14		1.05	30	70–72	78
15		3.05	20	164–166 ([22]: 163–165)	88
16		4.05	260	236–238	82

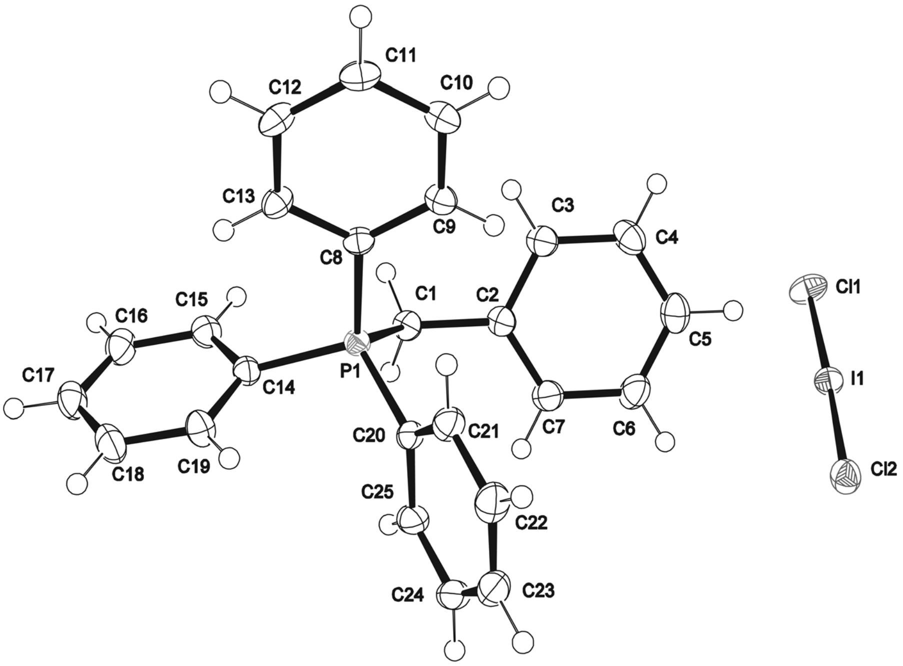


Fig. 1. *ORTEP Drawing of the molecule structure of* $BnPh_3P^+(ICl_2)^-$

Experimental Part

General. Iodine chloride (ICl; *Merck*, p.a.) was used without further purification. Solvents were dried and purified by standard methods. All chemicals were purchased from *Merck*. The reaction was followed by TLC monitoring the disappearance of starting materials. Some products are known and were characterized by comparison of their physical and spectroscopic data with those of authentic samples. M.p.: *Gallekamp* instrument; uncorrected. FT-IR Spectra: *BOMEM MB-100* instrument, found to be comparable with those reported; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance DRX 500* spectrometer at 500 and 125 MHz, resp.; δ in ppm rel. to Me_4Si as external standard, J in Hz. All the chemical shifts are quoted in ppm using the high-frequency positive convention. Elemental analyses: *Heraeus* CHN analyzer.

Benzyl(triphenyl)phosphonium Chloride (BTPPCl). To a 500-ml flask equipped with a magnetic stirrer were added BnCl (100 mmol, 12.65 g) and Ph_3P (100 mmol, 26.2 g) at 40–50°. The mixture was stirred for 20 min, cooled to r.t., and filtered. The filtered solid was washed with Et_2O (2×50 ml), crystallized, and identified.

Benzyl(triphenyl)phosphonium Dichloroiodate ($BTPPICl_2$). To ICl (16.2 g, 100 mmol) in CH_2Cl_2 (200 ml) was added at r.t. a soln. of $BnPh_3P^+Cl^-$ (33.88 g, 100 mmol) in CH_2Cl_2 (100 ml). After 50 min, Et_2O (100 ml) was added to the mixture, and the mixture was cooled and filtered. Recrystallization from Et_2O afforded 44.57 g (89%) of $BTTPPICl_2$. M.p. 164–166°. FT-IR (KBr): 3000–3150 (C–H, arom.), 2900–3000 (C–H, aliph.), 1480–1615 (C=C, arom), 700–750 (*arom.*). ^1H-NMR ($CDCl_3$): 4.74 (*d*, $J = 14.1$, $PhCH_2$); 6.96 (*d*, $^2J(H,P) = 7.00$, 2 arom. H); 7.19 (*d*, $J = 7.5$, 2 arom. H); 7.29 (*t*, $J = 7.8$, 1 arom. H); 7.57 (*dd*, $J_o = 7.8$, $^3J(H,P) = 12.4$, arom. H); 7.70 (*td*, $J_o = 7.5$, $^4J(H,P) = 3.5$, arom. H); 7.83 (*t*, $J = 7.4$, arom. H). Anal. calc. for $C_{25}H_{22}Cl_2IP$ (551.20): C 55.37, H 4.06; found: C 53.75, H 3.97.

General Procedure for 2,4,6-Triiodophenol (**1**). To a 250-ml flask equipped with a magnetic stirrer were added phenol (2 mmol) in CH_2Cl_2 (30 ml), MeOH (10 ml), $BTPPICl_2$ (6.1 mmol), and $NaHCO_3$ (2 g), and they were mixed at r.t. for 150 min. The progress of the reaction was monitored by TLC

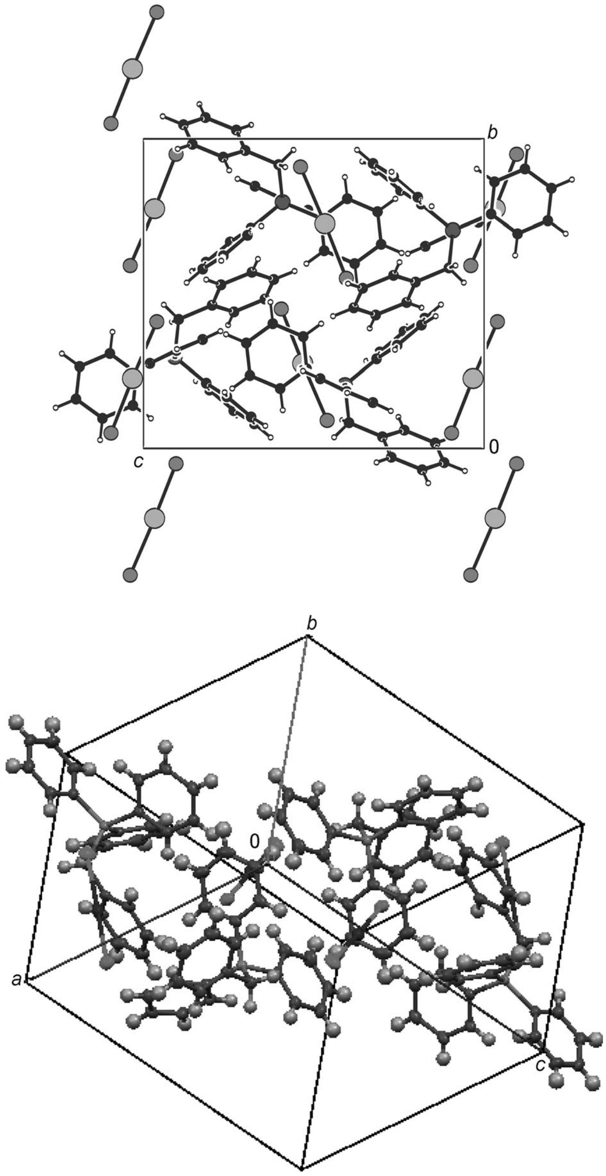


Fig. 2. *Two views of the unit cell of* $BnPh_3P^+(ICl_2)^-$

(AcOEt/hexane 2 : 1). After the completion, the mixture was filtered, and the liquid was neutralized by 5% $NaHCO_3$ and extracted with Et_2O (4 × 20 ml). The extracted org. layer was separated, dried (Na_2SO_4), and evaporated to afford the product. Recrystallization from aq. MeOH afforded 44.57 g (89%) of **1**. M.p. 155–157°. FT-IR (KBr): 3200–3500 (OH, phenol), 3050 (C–H, arom.), 1181 (C–O, phenol; C–OH, str.), 1623 and 1470 (C=C, arom., str.). ^{1}H-NMR ($CDCl_3$): 8.0 (*s*, 2 arom. H); 5.8 (*s*, OH).

Crystal Analysis of BTPPICl₂[1]). A yellow crystal of size $0.25 \times 0.20 \times 0.20$ mm^3 was used for intensity data set at 100(1) K on a *Bruker SMART 1000 CCD* area detector diffractometer. The intensity data were collected within the range $3.50° < \theta < 28.99°$ using graphite monochromated MoK_α radiation ($\lambda =$ 0.71073 Å). Accurate unit cell parameters and orientation matrix for data collection parameters, and orientation matrix for data collection were obtained from least-squares refinements. Intensities of 5393 reflections were measured, from which 699 reflections with $I > 2\sigma(I)$ were used in the refinement. *cf.* (*Table 2*). The crystal structure was solved by directed methods. Selected bond lengths and bond angles are given in *Table 3*.

Table 2. *Crystallographic Data and Structure Refinement of BTPPICl₂*

Empirical formula	$C_{25}H_{22}Cl_2IP$
M_r	551.20
Crystall dimensions [mm]	$0.25 \times 0.20 \times 0.20$
Temp. [K]	100.0(1)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	*P*21/n
Z	4
Unit cell parameters:	
a [Å]	12.4700(3)
b [Å]	13.2196(3)
c [Å]	14.4580(3)
β [°]	102.6340(10)
V [Å^3]	2325.67(9)
D_x [Mg m^{-3}]	1.574
Absorption coefficient [mm^{-1}]	1.685
F(000)	1096
θ Range for data collection [°]	3.50–28.99
Index ranges	$-12 \leq h \leq 12,\ -12 \leq k \leq 12,\ -7 \leq l \leq 7$
Reflections collected	5393
Independent reflections	716 (R(int) = 0.0344)
Completeness to $\theta = 28.99°$	99.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.488; 0.416
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	716/0/23
Goodness-of-fit on F^2	1.108
Final *R* indices (for 699 rfln. with $I > 2\sigma(I)$)	$R^1 = 0.0637$, $wR^2 = 0.0954$
R Indices (all data)	$R^1 = 0.0390$, $wR^2 = 0.0870$
Absolute structure parameter	−0.03(7)
Largest diff. peak and hole [e Å^{-3}]	1.587; −0.842

X-Ray Data Collection, Structure Determination, and Refinement Procedures. The structure has been solved by direct methods and refined by full-matrix-least squares techniques on F^2. All non-H-atoms were filtered anisotropically. The position of H-atom was assigned an isotropic thermal parameter. The values of *R*, *wR* with a goodness of fit on F^2 of 1.108 are 0.0390 and 0.0870, resp. The final difference density map showed a maximum peak and hole of 1.587 and −0.842 e Å^{-3}. All structural calculations

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[1]) CCDC-698883 contains the supplementary crystallographic data for BTPPICl₂. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 3. *Bond Lengths and Angles for BTPPICl$_2$*a))

Bond lengths [Å]		Bond angles [°]	
I(1)–Cl(1)#1	2.6284(5)	Cl(1)#1–I(1)–Cl(1)	178.220(15)
I(1)–Cl(1)	2.4980(5)	C(8)#2–P(1)–C(1)#3	112.83(8)
P(1)–C(1)#2	1.8189(17)	C(14)#2–P(1)–C(1)	107.33(8)
P(1)–C(1)#3	1.7914(16)	C(20)#3–P(1)–C(1)	110.56(8)
P(1)–C(1)	1.7918(16)	C(14)#2–P(1)–C(20)#4	109.44(8)
P(1)–C(1)#4	1.7949(16)	C(8)#3–P(1)–C(20)#4	108.78(8)
C(1)–H(1A)	0.9700	C(8)–P(1)–C(14)#4	107.81(7)
C(1)–H(1B)	0.9700	P(1)–C(1)–H(1A)	108.4
		P(1)–C(1)–H(1B)	108.4
		H(1A)–C(1)–H(1B)	107.5

a) Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+1, z$; #2 $-x+2, -y, z$; #3 $y+1, -x+1, -z$; #4 $-y+1, x-1, -z$.

were carried out with SHELXTL V. 5.10 structure determination software; intensity data were collected on a *Siemens SMART CCD* diffractometer with graphite-monochromated MoK_α radiation. The compound crystallized in the symmetric space group *P*21/*n* that belongs to the monoclinic system.

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